

## PATENT ABSTRACTS OF JAPAN

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## (54) THERMAL RECORDING MATERIAL

## (57)Abstract:

PURPOSE: To provide thermal recording material in which sensitivity is high and meservability is good and suitability for offset printing having picking resistance is excellent.

CONSTITUTION: Thermal recording paper is constituted by providing an undercoating layer containing organic and/or inorganic pigment and adhesive resin on a sheetlike supporting body and providing a thermal coloring layer which contains colorless or light-colored electron suppliable coloring dye, an electron acceptable color developing compound for coloring dye by heating and adhesive resin as a main component and a protective layer on the undercoating layer. In the thermal recording paper, the protectively layer contains polyvinyl alcohol having  $\geq 1000$  degree of polymerization and  $\geq 98\%$  degree of saponification, so that the weight ratio after drying is 20-50wt.% of the whole protective layer. Furthermore the undercoating layer contains a starch-polyvinyl acetate graft copolymer and/or its partially saponified substance, so that the weight ratio after drying is 10-30wt.% of the whole undercoating layer.

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**CLAIMS**

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[Claim(s)]

[Claim 1] a sheet-like base material top — organic — and — or the under coat containing an inorganic pigment and adhesives resin — preparing — a it top — the electron-donative color-enhancing color of colorlessness thru/or light color — In the thermographic recording paper which prepared the sensible-heat coloring layer and protective layer which contain the electronic receptiveness development nature compound made to color this color-enhancing color with heating, and adhesives resin as a principal component In the whole protective layer, the weight ratio after drying 98% or more of polyvinyl alcohol contains [ said protective layer ] 20 to 50% of the weight 1000 or more degrees of polymerization and whenever [ saponification ]. and said under coat — as adhesives resin — a starch-polyvinyl acetate graft copolymer — and — or the thermal recording ingredient with which the weight ratio after drying the partial saponification object is characterized by the whole under coat containing ten to 30% of the weight.

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[Translation done.]

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a thermal recording ingredient. Furthermore, shelf life is good in detail at high sensitivity, and it is related with the thermal recording ingredient which has offset-printing fitness with picking-proof nature.

[0002]

[Description of the Prior Art] A thermal recording ingredient can prepare the sensible-heat coloring layer which contains a color-enhancing color like an electron-donative leuco color, development nature compounds, such as a phenol nature compound of electronic receptiveness, and adhesives resin as a principal component on the sheet-like base material which generally consists of paper, a synthetic paper, or plastic film, can make these color-enhancing color and a developer able to react with heat energy, and can obtain a coloring record image. On the other hand, a coloring image is obtained only by heating, and the advantage of being able to make this recording device compact comparatively easily is esteemed, and thermal recording is broadly used as various information recording methods, such as facsimile, an automatic ticket vending machine, a science instrumentation, CD/ATM, and a printer for POS labels.

[0003] In addition to high shelf life, printing nature has been required with the breadth of such an application. In order to acquire high shelf life, generally preparing a protective layer on a sensible-heat layer is performed (a Japanese Patent Publication No. 44 No. -27880 official report, Provisional-Publication-No. 48 No. -51644 official report). However, if such a protective layer is prepared on a sensible-heat layer, since conduction of the heat to the sensible-heat layer from a thermal head will pass a protective layer and will reach, a sensibility fall is unavoidable. Then, since this sensibility fall is prevented, it is possible to make it a base material with low thermal conductivity (Provisional-Publication-No. 55 No. -164192 official report). That is, an under coat is prepared and this under coat is used as the layer with many openings. When it prints to the thermographic recording paper of the lamination which has such a porous under coat, it will become weak to a picking.

[0004]

[Problem(s) to be Solved by the Invention] This invention relates to a thermal recording ingredient. Furthermore, shelf life is good in detail at high sensitivity, and it is in offering the thermal recording ingredient which has offset-printing fitness with picking-proof nature.

[0005]

[Means for Solving the Problem] the purpose of this invention — a sheet-like base material top — organic — and — or the under coat containing an inorganic pigment and adhesives resin — preparing — a it top — the electron-donative color-enhancing color of colorlessness thru/or light color — In the thermographic recording paper which prepared the sensible-heat coloring layer and protective layer which contain the electronic receptiveness development nature compound made to color this color-enhancing color with heating, and adhesives resin as a principal component In the whole protective layer, the weight ratio after drying 98% or more of polyvinyl alcohol contains [ said protective layer ] 20 to 50% of the weight 1000 or more degrees of polymerization and whenever [ saponification ]. and said under coat — as adhesives resin — a starch-polyvinyl acetate graft copolymer — and — or the weight ratio after drying the partial saponification object was attained by the thermal recording ingredient characterized by the whole under coat containing ten to 30% of the weight.

[0006] In the protective layer, 1500 or more degrees of polymerization and whenever [ saponification ], although the weight ratio of shelf life after drying 98% or more of polyvinyl alcohol improved by leaps and bounds by [ of the whole protective layer ] containing 20% of the weight or more, the picking at the time of printing got worse as a result of the improvement of film forming ability of a protective layer. In order to work on a cure about this, the adhesives resin which the porous stratification is made, and comes as adhesives resin of an under coat at the time of paint film formation, and can aim at improvement in bond strength was chosen. consequently, a starch-polyvinyl acetate graft copolymer — and — or it found out that the picking at the time of printing could be solved without causing the fall of sensibility by containing in the range whose weight ratio after drying the partial saponification object is 10 - 30% of the weight of the whole under coat. however, a starch-polyvinyl acetate graft copolymer — and — or less than 10% of the weight of the whole under coat of the paint film reinforcement of an under coat was [ the weight ratio after the partial saponification object drying ] insufficient, and the picking occurred at the time of printing. however, a starch-polyvinyl acetate graft copolymer — and — or when there are more whole under coats than 30 % of the weight and the weight ratio after drying the partial saponification object blended, sensibility fell. The thermographic recording paper obtained by this invention was able to be used as the record ingredient which is excellent in the shelf life and sensibility which were not conventionally, and has the good quality of the picking at the time of printing again.

[0007] the thing which made the modified starch which received one or more sorts of denaturation chosen from natural starch, a natural starch inclusion, the amylose by which fractionation was carried out, amylopectins and those etherification starch, esterification starch, bridge formation starch, graft conversion starch, oxidization starch, dextrin starch, acid-treatment starch, and enzyme conversion starch consider vinyl acetate or other vinyl ester as the starch-polyvinyl acetate graft copolymer in this invention, and/or its saponification object — and — or that to which the vinyl acetate part which carried out the graft saponified is included.

[0008] moreover — as the adhesives of an under coat — a starch-polyvinyl acetate graft copolymer — and — or in order to raise the water resisting property of an under coat in addition to the partial saponification object, an aqueous emulsion is used and a thing as specifically shown below is mentioned. An SBR latex, a polystyrene acrylic ester emulsion, a polyvinyl acetate emulsion,

etc. are mentioned. When it combined with an SBR latex with many gel contents especially, the result good to the improvement in sensibility was shown in the waterproof improvement in a paint film, and coincidence. The under coat in this invention consists of a bulking agent and adhesives resin as a principal component, inorganic and the organic pigment which are used for the object for general paper manufacture and coating as a bulking agent are used for arbitration, and the following is specifically mentioned. For example, organic system resin impalpable powder, such as urea-formalin resin, styrene / methacrylic-acid copolymer, and polystyrene resin, etc. is in inorganic system impalpable powder, such as clay, a calcium carbonate, a magnesium carbonate, talc, a silica, the diatom earth, synthetic aluminum silicate, a zinc oxide, titanium oxide, an aluminum hydroxide, a barium sulfate, a calcium carbonate by which surface treatment was carried out, and a silica, and a list.

[0009] The rate of a compounding ratio of the bulking agent and binder of this undercoat is decided to be arbitration by the selected component, and, generally is between 20:1-1:1. Into an under coat, a thickener, fluorescent dye, a coloring color, a color pigment, a surfactant, an ultraviolet-rays inhibitor, a dispersant, a wax, an antioxidant, metallic soap, etc. can be blended in the range which does not spoil the effectiveness of this invention other than an above-mentioned bulking agent and a binder. In forming this undercoat, 1 - 15 g/m<sup>2</sup> (dry weight) of coverage is common, and although that coating is easily performed by applying to a paper base material using the usual coater, it is desirable to carry out coating by the coating method which can form a blade and the good coating layer of front-face nature called a slit die preferably.

[0010] Therefore, the sensible-heat coloring layer formed on an under coat is formed in a conventional method. If used for the electron-donative color-enhancing color and the common pressure sensitive paper which are used for this invention, a thermographic recording paper, etc., there will be especially no limit. The electron-donative color-enhancing color of white and light color can be used. Specifically for example, for example A 2 and 2 screw [4-[phtalide -3 and 6'-(N-cyclohexyl-N-methylamino)-3'-methyl SUPIRO [9'-xanthene]-2'-IRUAMIDO] phenyl] propane, 3-diethylamino-6-methyl-7-anilino fluoran, 3-piperidino-6-methyl-7-anilino fluoran, 3-(N-methyl-N-cyclohexylamino)-6-methyl-7-anilino fluoran, 3-diethylamino-7-chloroanilino fluorane, 3-[N-ethyl-N-(p-methylphenyl) amino]-6-methyl-7-anilino fluoran, 3-diethylamino-7-(meta-trifluoromethyl) anilino fluoran, 3-(N-ethyl-N-tetrahydrofurfuryl) amino-6-methyl-7-anilino fluoran, It is the thing of fluoran system colors, such as 3-(N-ethyl-N-isopentyl) amino-6-methyl-7-anilino fluoran and 3-dibutylamino-6-methyl-7-anilino fluoran, which consists of 1 member at least.

[0011] The electronic receptiveness acid used for this invention is liquefied or evaporated above 70 degrees C, reacts with said color-enhancing color, and makes this color preferably beyond ordinary temperature. As electronic receptiveness acid, for example 4 and 4'-screw (p-toluenesulfonyl amino carbonylamino) diphenylmethane, A - isopropylidene diphenol, and 4 and 4' 4, 4'-isopropylidene screw (2-chlorophenol), A - isopropylidene screw (2-methyl phenol), and 4 and 4' 4, 4'-isopropylidene screw (2, 6-tert-butylphenol), -sec-butylidene diphenol, and 4 and 4' 4, 4'-cyclohexylidene diphenol, 4-tert-butylphenol, 4-phenylphenol, 4-hydroxy diphenoxide, A naphthol, the beta-naphthol, methyl-4-hydroxy benzoate, A 4-hydroxy-acetophenone, a salicylic-acid anilide, a novolak mold phenol, A halogenation novolak mold phenol resin, 4, and 4'-thio screw (3-methyl-6-tert-butylphenol), P-hydroxybenzoic-acid propyl, P-hydroxybenzoic-acid isopropyl, P-hydroxybenzoic-acid butyl, P-hydroxybenzoic-acid benzyl, P-hydroxybenzoic-acid methylbenzyl, oxalic acid, a maleic acid, a tartaric acid, Aliphatic carboxylic acid, such as a citric acid, a succinic acid, and stearin acid, a benzoic acid, A p-tert-butyl benzoic acid, a phthalic acid, a gallic acid, a salicylic acid, 3-isopropyl salicylic acid, 3, a 5-G alpha-methylbenzyl salicylic acid, A screw (4-hydroxyphenyl) sulfide, 1, 7-JI (4-hydroxy phenylthio) -3, 5-dioxa heptane, With p-nitrobenzoic acid and these organic developer, for example, zinc, magnesium, A salt with polyvalent metal, such as aluminum, calcium, titanium, manganese, tin, and nickel, 4 and 4'-dihydroxy diphenylsulfone, 2, 4-dihydroxy diphenylsulfone, 3, 3'-dihydroxy diphenylsulfone, 3, the 3'-diamino -4, 4'-dihydroxy diphenylsulfone, 3, 3'-diaryl -4, 4'-dihydroxy-diphenylsulfone, 3, 3'-dichloro -4, 4'-dihydroxy diphenylsulfone, 4-hydroxy-diphenylsulfone, 4-hydroxy-4'-isopropyl diphenylsulfone, 4-hydroxy-4'-isopropoxy diphenylsulfone and 4-hydroxy-4'-benzyloxy diphenylsulfone, 2, 4-dihydroxy diphenylsulfone, 2, 4'-dihydroxy -4'-methyl diphenylsulfone, It is the thing which was chosen from 3, 4-dihydroxy phenyl-p-tris RUHON, the N-(o-toluoyl)-p-toluene sulfo amide, the N-(p-tosyl)-N'-phenyl urea, etc. and which consists of 1 member at least.

[0012] the electronic receptiveness acid — usually — the color-enhancing color 1 weight section — receiving — 1 - 5 weight section — it is used, 1.5 - 3 weight section's coming out comparatively preferably, and mixing. moreover — this invention — the need — responding — the aromatic series ether and ester — and — or sensitizers, such as an aliphatic series amide or ureido, — For example, oxalic acid G p-methylbenzyl ester, oxalic acid G p-chloro benzyl ester, Dimethyl terephthalate ester, terephthalic-acid dibutyl ester, 4-ethoxy phenyl 4'-chloro benzyl ether, Terephthalic-acid dibenzyl ester, isophthalic acid dibutyl ester, 1-hydroxy naphthoic-acid phenyl ester, 1, 2-JI (3-methylphenoxy) ethane, 1, 2-JIFENOKISHI ethane, 1-phenoxy-2-(4-methylphenoxy) ethane, Diphenyl carbonate, diphenylsulfone, p-benzyl biphenyl, 2, and 2'-methylenebis (4-methyl-6-t-butylphenol), 4 and 4'-butylidenebis (6-t-butyl-3-methyl phenol), 1, 1, 3-tris (2-methyl-4-hydroxy-5-t-butylphenyl) butane, 2 and 2'-methylenebis (4-ethyl-6-t-butylphenol), Hindered phenols, such as a 2, 4-G t-butyl-3-methyl phenol, 4, and 4'-thio screw (3-methyl-6-t-butylphenol), 2 -(2'-hydroxy-5'-methylphenyl)- Benzotriazol, a 2-hydroxy-4-benzyloxy benzophenone, etc. are mentioned.

[0013] it is mixed and used, and independence or in order to acquire sufficient heat responsibility, it is desirable still more desirable to carry out 3 weight sections use from 0.2 to the electron-donative color-enhancing color 1 weight section, and it boils, these heat fusibility matter, i.e., sensitizer, it receives, and is the 0.5 to 2.0 weight section. Distribution of these materials, an electron-donative color-enhancing color, the electronic receptiveness acid, and a sensitizer is performed with water soluble resin. Various wet grinding mills, such as a Sand grinder, attritor, a ball mill, and a Cobot mill, distribute each material as a dispersion-medium object using water with a surfactant besides water-soluble synthetic high polymers, such as polyacrylamide, a polyvinyl pyrrolidone, polyvinyl alcohol, a carboxymethyl cellulose, styrene maleic anhydride copolymer salts, and those derivatives, etc. In addition to both an electron-donative color-enhancing color, and electronic receptiveness both [ either or ], it distributes to coincidence, or depending on the case, an eutectic object may be created beforehand and a sensitizer may distribute.

[0014] In this invention, waxes, metallic soap, an ultraviolet ray absorbent, a shelf-life improver, fluorescent dye, etc. can be mentioned adhesives resin, inorganic or an organic pigment, and also if needed as an ingredient which otherwise constitutes a sensible-heat coloring layer.

[0015] The thing with the adhesives resin generally known as adhesives resin to combine is possible. As the example, polyvinyl alcohol, carboxy group denaturation polyvinyl alcohol, Aceto acetyl group denaturation polyvinyl alcohol, cation radical denaturation polyvinyl alcohol, Sulfone radical denaturation polyvinyl alcohol, silica denaturation polyvinyl alcohol, Starch and its derivative, gum arabic, gelatin, casein, methyl cellulose, Hydroxyethyl cellulose, a hydroxymethyl cellulose, a polyvinyl pyrrolidone, Polyacrylate, poly acrylamide, a styrene maleic anhydride copolymer, Water soluble resin, such as a methyl-vinyl-ether-maleic-anhydride copolymer and an isopropanal pyrene-maleic-anhydride copolymer, A styrene-butadiene latex, a vinyl acetate-acrylic ester copolymerization

emulsion, Water-dispersion resin, such as a polyurethane emulsion, a polyvinyl chloride emulsion, a polyvinylidene chloride emulsion, a methacrylic ester copolymerization emulsion, and an emulsion of an acrylic ester copolymer, can be used. Moreover, in order to make the water resisting property of a paint film firm, it can use combining a cross linking agent.

[0016] As a cross linking agent, inorganic compounds, such as ammonium persulfate, and a ferric chloride, a magnesium chloride, or a boric acid, and a borax can be used for diglycidyl system compounds, such as polyamine system compounds, such as multiple-valued aldehyde system compounds, such as glyoxal, a glutaraldehyde, and dialdehyde starch, and polyethyleneimine, an epoxy system compound, polyamide resin, and glycerol diglycidyl ether, a dimethylol urea compound, and a list.

[0017] As a pigment, organic system resin impalpable powder, such as urea-formalin resin, styrene / methacrylic-acid copolymer, and polystyrene resin, can be raised to inorganic system impalpable powder, such as clay, a calcium carbonate, a magnesium carbonate, talc, a silica, the diatom earth, synthetic aluminum silicate, a zinc oxide, titanium oxide, an aluminum hydroxide, a barium sulfate, a calcium carbonate by which surface treatment was carried out, and a silica, and a list, for example.

[0018] As metallic soap, a higher-fatty-acid metal salt is used and zinc stearate, calcium stearate, aluminum stearate, etc. are mentioned. As a wax, paraffin wax, polyethylene wax, carnauba wax, a micro crystallin wax, Kandy Lynn Waxes, a montan wax, a fatty-acid amide system wax, etc. are mentioned.

[0019] A sensible-heat coloring layer coating is applied so that it may become 3 - 8 g/m<sup>2</sup> (desiccation) on one front face of a sheet-like base material, and a heat-sensitive recording layer is formed of it. In the protective layer prepared on a sensible-heat coloring layer, a dry pick can be pressed down without the weight ratio after drying 98% or more of polyvinyl alcohol affecting impression of shelf life and printing ink 1500 or more degrees of polymerization and whenever [ saponification ], by [ of the whole protective layer ] containing 20 to 50% of the weight. The combination fewer than 20 % of the weight of coat formation of a protective layer is inadequate, and shelf life falls by it. Moreover, when blended more mostly than 50 % of the weight, the width of face of the printing conditions at the time of offset printing became narrow, printed, and became that of \*\* potatoes. It will be in the condition that this has the narrow water width as used in the field of the printing industry, and if the dampening water amount of supply is made [ many ] in order to suppress the printing greasing of the non-streak section at the time of printing, the poor repeatability of the concentration nonuniformity of the image section or a halftone dot configuration will become easy to generate easily, and the water defeat phenomenon in emulsification ink will happen. if the dampening water amount of supply must be lessened slightly for this reason, but lessening the dampening water amount of supply slightly, and operating the offset press requires skill and it lessens it too much — generating of a greasing — when many [ too ], there was generating of water defeat, and it printed very much and changed into the \*\*\*\*\* condition. In the range which does not check the effectiveness of this invention 1500 or more degrees of polymerization and whenever [ saponification ] as adhesives resin in a protective layer other than 98% or more of polyvinyl alcohol, aceto acetylation polyvinyl alcohol, Denaturation polyvinyl alcohol, such as carboxyl denaturation polyvinyl alcohol, Starch, casein, gelatin, glue, a polyamide, polyacrylamide, It can blend combining hydroxyethyl cellulose, methyl cellulose, a cull BOKIME chill cellulose, a hydronalium KIPURO pill cellulose, a styrene maleic anhydride copolymer salt, a diisobutylene-maleic-anhydride copolymer salt, etc.

[0020] Inorganic pigments, such as a calcium carbonate, clay, a baking kaolin, talc, titanium oxide, a magnesium carbonate, a zinc oxide, an aluminum silicate, a calcium silicate, a silica, and an aluminum hydroxide, a starch grain child, wheat flour, silicon resin, a urea and formalin resin, phenol resin, melamine formalin resin, an epoxy resin, guanamine formalin resin, polystyrene resin, etc. can be used together as a pigment. Moreover, according to the approach of this invention, a protective layer can improve a water resisting property further especially for the application of which an advanced water resisting property is required by using together cross linking agents, such as a melamine, epoxy, an aziridine, glyoxal, dimethylol urea, the poly aldehyde, a boric acid, a borax, and a zirconium salt, for example, although sufficient water resisting property can be given.

[0021] Into a protective layer, the wax and metallic soap which were illustrated below if needed can be blended. A higher-fatty-acid amide, for example, octadecanamide, besides paraffin wax, a cull navarro wax, a micro crystallin wax, and polyethylene wax, ethylene bis-octadecanamide, higher-fatty-acid ester, higher-fatty-acid polyvalent metallic salt, i.e., zinc stearate, aluminum stearate, calcium stearate, zinc oleate, etc. are mentioned. Putting in various additives, such as an oil repellent agent, a defoaming agent, a viscosity modifier, a surfactant, fluorescent dye, an ultraviolet ray absorbent, a coloring color, and a color pigment, in the range which otherwise does not spoil the effectiveness of this invention does not interfere.

[0022] a protective layer — dry weight — it is — 0.1 - 6 g/m<sup>2</sup> — 0.5-4 g/m<sup>2</sup> coating is carried out more preferably. In less than two 0.1 g/m, if it is deficient in the effectiveness as a protective layer and 6 g/m<sup>2</sup> is exceeded, it will become the cause that coloring sensibility falls. Moreover, a protective layer can also be made into the multilayer more than two-layer.

[0023] There is no limitation according to rank in the base material ingredient used for this invention, for example, it can use suitably paper of fine quality, a report grade paper, coat paper, art paper, cast coated paper, a resin laminated paper, a polyolefine system synthetic paper, a synthetic fiber paper, a synthetic-resin film, etc. for it. As an approach of forming a sensible-heat coloring layer, any of the known methods of application, such as the Ayr knife method, the blade method, the gravure method, the roll coater method, a spray method, a dip method, the bar method, and the extrusion method, may be used. Moreover, although the same coating method as the approach of forming a sensible-heat coloring layer as an approach of forming a protective layer is held, they are the Ayr knife method, the gravure method, the roll coater method, and a spray method.. The approach of writing lightly the protective layer coating which carried on a sensible-heat coloring layer like a dip method and the extrusion method is desirable. Osmosis of the oil from a rear face or a plasticizer can be suppressed, or a back layer can also be prepared for curl control.

[0024]

[Example] An example explains this invention still more concretely below.

Preparation of the formation (1) pigment dispersion liquid of example 1 under coat Amount (% of the weight)

Baking clay 30 (en gel heart company make, trade name ANSI REXX 93)

47 % of the weight liquid of polystyrene particles 25 (the Mitsui Toatsu Chemicals, Inc. make, trade name gross DERU104s)

20 % of the weight liquid of starch-vinyl acetate graft copolymerization resin 38 (Japanese dregs chemistry company make, trade name PETOKOTO c8)

Carboxymethyl cellulose 0.5 (the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, trade name AG gum)

40 % of the weight liquid of sodium polyacrylate 0.3 (the Kao Corp. make, trade name poise 520)

Defoaming agent 0.02 (the Sannopuko make, a trade name DF 122)

After the homogenizer distributed for 5 minutes, it blended 6 % of the weight (the Asahi Chemical Co., Ltd. make, trade name L1537) of 50 % of the weight liquid of SBR latexes, and considered as the coating for under coats. 8 g/m<sup>2</sup> (desiccation) coating of this coating liquid was carried out in the high-quality paper of basis-weight 40 g/m<sup>2</sup> by the chip blade method, and the under coat was

formed.

[0025]

Formation of a sensible-heat layer (1) Preparation of color-enhancing color dispersion liquid A Component Amount (% of the weight)

3-dibutylamino-6-methyl-7-ANIRINO 40 Fluoran Polyvinyl alcohol 10% liquid 40 (polymerization degree 500, whenever [ saponification ] 90%)

Water 20 (2) Preparation of development nature compound dispersion liquid B Component Amount (% of the weight)

4 and 4'-dihydroxy diphenylsulfone 40 Polyvinyl alcohol 10% liquid 40 (polymerization degree 500, whenever [ saponification ] 90%)  
Water 20 [0026]

(3) Preparation of sensitizer dispersion liquid C Component Amount (% of the weight)

Oxalic acid G p-methylbenzyl ester 40 Polyvinyl alcohol 10% liquid 40 (polymerization degree 500, whenever [ saponification ] 90%)

Water 20 (4) Preparation of shelf-life improver dispersion liquid D Component Amount (% of the weight)

4-(2-methyl-glycidyoxy)-4'- 40 Benzyloxy diphenylsulfone Polyvinyl alcohol 10% liquid 40 (polymerization degree 500, whenever [ saponification ] 90%)

water 20 — these constituents were separately distributed in the vertical mold sand mill (the product made from eye MEKKUSU, Sand grinder).

(5) Preparation of pigment dispersion liquid E Component Amount (% of the weight)

Precipitated calcium carbonate 40 (the product made from \*\* Co. in Shiroishi, brilliant 15)

0.7% solution of sodium hexametaphosphate 60 — this constituent was distributed by the cow loess disperser.

[0027] Furthermore, it is 10% starch-vinyl acetate graft copolymerization resin as 20% octadecanamide distribution object and adhesives H as distributed object F liquid as 49% of styrene butadiene latex (the Sumitomo Dow-Jones company make, trade name P0Y72), and adhesives I as 20% zinc stearate distribution object and distributed object G liquid. (Japanese dregs chemistry company make, trade name PETOKOTO c8) It prepared. Using these distributed objects and adhesives, the weight ratio after desiccation blended so that it might be set to A:B:C:D:E:F:G:H:I=10:20:20:3:22:5:5:1 0.5, and it considered as coating liquid. 6 g/m2 (desiccation) coating of this coating liquid was carried out on the above-mentioned under coat by the rod blade method, and the sensible-heat coloring layer was formed.

[0028] As the formation adhesives resin (A, B) of a protective layer whenever [ a degree of polymerization 1700 and / saponification. ] — 99.5% polyvinyl alcohol (Kuraray Make —) Trade name OTP4H, acrylic emulsion resin (the Mitsui Toatsu Chemicals make, trade name barrier star B1850), As a pigment (C), fines silicic acid (the product made from the Mizusawa chemistry, trade name Ms. KASHIRU P603), Protective layer coating liquid is prepared so that a dry weight ratio may be set to A:B:C:D=40:10:40:10 using zinc stearate (D) 20 more%. After 2 g/m2 (desiccation) spreading and desiccation, 5 – 8% of moisture, and linear pressure 80 kg/cm performed the calendaring with the rod blade on the sensible-heat coloring layer of the sensible-heat coloring paper which formed this previously, and the thermal recording ingredient was created.

[0029] Example of a comparison Except having made 38 % of the weight (Japanese dregs chemistry company make, trade name PETOKOTO c8) of 20 % of the weight solutions of starch-vinyl acetate graft copolymerization resin of the under coat in one example 1 into 18 % of the weight, and having made baking clay (en gel heart company make, trade name ANSI REXX 93) into 55 % of the weight, same processing was performed and the thermal recording ingredient was created.

[0030] Example of a comparison The degree of polymerization 1700 of the protective layer in two examples 1, whenever [ saponification ] 99.5% Except having made 40 % of the weight (Kuraray Make, trade name OTP4H) of polyvinyl alcohol into 15 % of the weight, and having made fines silicic acid (the product made from the Mizusawa chemistry, trade name Ms. KASHIRU P603) into 65 % of the weight from 40 % of the weight, same processing was performed and the thermal recording ingredient was created.

[0031] Example of a comparison Except having combined the same protective layer as the same under coat as the example 1 of 3 comparisons, and the example 2 of a comparison, the same processing as an example 1 was performed, and the thermal recording ingredient was created.

[0032]

[Table 1]

	感 度	耐ホリ塩化ビニルラ フ性 ( 保存率 % )	印刷水負け 評価	ドライビタの 評価
実施例 1	1. 3 3	9 8	○	○
比較例 1	1. 3 2	9 3	○	×
比較例 2	1. 1 1	6 5	×	○
比較例 3	1. 1 5	6 1	×	×

[0033] as the adhesives resin of a protective layer — whenever [ 1000 or more degrees of polymerization and / saponification ] — 98% or more of polyvinyl alcohol — as 20 to 50 weight section implication, and the adhesives resin of an under coat — water soluble resin — a starch-polyvinyl acetate graft copolymer — and — or by carrying out 30 weight sections content of the partial saponification object from 10, shelf life was good at high sensitivity, and the good thing of offset-printing fitness with picking-proof nature was obtained.

[0034] Sensitometry : system sensible-heat facsimile was measured using what was converted into the trial. Pulse width was modulated on 10ms/line of one-line chart lasting time, and the conditions of 8\*8 dots/mm of scanning density, the impression energy per dot was adjusted to 0.5ms, and printing of 64 lines was performed. The coloring concentration in that case was measured by Macbeth concentration meter RD-514, and it considered as the value representing record sensibility.

[0035] Polyvinyl chloride-proof lap nature : The printing object which evaluated record sensibility was stuck on the polyvinyl chloride wrap film, it covered with the polyvinyl chloride wrap film from on the further, and the printing concentration after one-

week progress was measured at 40 degrees C Macbeth concentration meter RD-514. The rate of preservation was computed from change of printing concentration, and extent of polyvinyl chloride-proof lap nature was evaluated.

[0036] Printing water defeat trial : After ink's having added 0.5 cc of water to ink 0.25g with \*\*\*\* coloring matter best KYUA RNC-red (tuck 6) using the \*\*\*\*\* RI circuit tester, scouring ink and water for 1 minute with the ink kneading roller and making ink emulsify, it evaluated by performing a printing trial.

O x which ink transferred to paper good Transition of ink was not appropriate. [0037] Dry pick trial : Using a \*\*\*\*\* RI circuit tester, ink adds ink 0.25g with \*\*\*\* coloring matter best KYUA RNC-red (tuck 15), and scours ink and water for 1 minute with an ink kneading roller. The printing trial was performed after making ink emulsify.

O x in which a paint film did not exfoliate at the time of printing A paint film did not exfoliate at the time of printing. [0038]

[Effect of the Invention] Shelf life was good at high sensitivity, and this invention enabled it to manufacture the good thing of offset-printing fitness with picking-proof nature.

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**TECHNICAL FIELD**

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[Industrial Application] This invention relates to a thermal recording ingredient. Furthermore, shelf life is good in detail at high sensitivity, and it is related with the thermal recording ingredient which has offset-printing fitness with picking-proof nature.

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PRIOR ART

[Description of the Prior Art] A thermal recording ingredient can prepare the sensible-heat coloring layer which contains a color-enhancing color like an electron-donative leuco color, development nature compounds, such as a phenol nature compound of electronic receptiveness, and adhesives resin as a principal component on the sheet-like base material which generally consists of paper, a synthetic paper, or plastic film, can make these color-enhancing color and a developer able to react with heat energy, and can obtain a coloring record image. On the other hand, a coloring image is obtained only by heating, and the advantage of being able to make this recording device compact comparatively easily is esteemed, and thermal recording is broadly used as various information recording methods, such as facsimile, an automatic ticket vending machine, a science instrumentation, CD/ATM, and a printer for POS labels.

[0003] In addition to high shelf life, printing nature has been required with the breadth of such an application. In order to acquire high shelf life, generally preparing a protective layer on a sensible-heat layer is performed (a Japanese Patent Publication No. 44 No. -27880 official report, Provisional-Publication-No. 48 No. -51644 official report). However, if such a protective layer is prepared on a sensible-heat layer, since conduction of the heat to the sensible-heat layer from a thermal head will pass a protective layer and will reach, a sensibility fall is unavoidable. Then, since this sensibility fall is prevented, it is possible to make it a base material with low thermal conductivity (Provisional-Publication-No. 55 No. -164192 official report). That is, an under coat is prepared and this under coat is used as the layer with many openings. When it prints to the thermographic recording paper of the lamination which has such a porous under coat, it will become weak to a picking.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] Shelf life was good at high sensitivity, and this invention enabled it to manufacture the good thing of offset-printing fitness with picking-proof nature.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] This invention relates to a thermal recording ingredient. Furthermore, shelf life is good in detail at high sensitivity, and it is in offering the thermal recording ingredient which has offset-printing fitness with picking-proof nature.

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## MEANS

[Means for Solving the Problem] the purpose of this invention — a sheet-like base material top — organic — and — or the under coat containing an inorganic pigment and adhesives resin — preparing — a it top — the electron-donative color-enhancing color of colorlessness thru/or light color — In the thermographic recording paper which prepared the sensible-heat coloring layer and protective layer which contain the electronic receptiveness development nature compound made to color this color-enhancing color with heating, and adhesives resin as a principal component In the whole protective layer, the weight ratio after drying 98% or more of polyvinyl alcohol contains [ said protective layer ] 20 to 50% of the weight 1000 or more degrees of polymerization and whenever [ saponification ]. and said under coat — as adhesives resin — a starch-polyvinyl acetate graft copolymer — and — or the weight ratio after drying the partial saponification object was attained by the thermal recording ingredient characterized by the whole under coat containing ten to 30% of the weight.

[0006] In the protective layer, 1500 or more degrees of polymerization and whenever [ saponification ], although the weight ratio of shelf life after drying 98% or more of polyvinyl alcohol improved by leaps and bounds by [ of the whole protective layer ] containing 20% of the weight or more, the picking at the time of printing got worse as a result of the improvement of film forming ability of a protective layer. In order to work on a cure about this, the adhesives resin which the porous stratification is made, and comes as adhesives resin of an under coat at the time of paint film formation, and can aim at improvement in bond strength was chosen. consequently, a starch-polyvinyl acetate graft copolymer — and — or it found out that the picking at the time of printing could be solved without causing the fall of sensibility by containing in the range whose weight ratio after drying the partial saponification object is 10 - 30% of the weight of the whole under coat. however, a starch-polyvinyl acetate graft copolymer — and — or less than 10% of the weight of the whole under coat of the paint film reinforcement of an under coat was [ the weight ratio after the partial saponification object drying ] insufficient, and the picking occurred at the time of printing. however, a starch-polyvinyl acetate graft copolymer — and — or when there are more whole under coats than 30 % of the weight and the weight ratio after drying the partial saponification object blended, sensibility fell. The thermographic recording paper obtained by this invention was able to be used as the record ingredient which is excellent in the shelf life and sensibility which were not conventionally, and has the good quality of the picking at the time of printing again.

[0007] the thing which made the modified starch which received one or more sorts of denaturation chosen from natural starch, a natural starch inclusion, the amylose by which fractionation was carried out, amylopectins and those etherification starch, esterification starch, bridge formation starch, graft conversion starch, oxidization starch, dextrin starch, acid-treatment starch, and enzyme conversion starch consider vinyl acetate or other vinyl ester as the starch-polyvinyl acetate graft copolymer in this invention, and/or its saponification object — and — or that to which the vinyl acetate part which carried out the graft saponified is included.

[0008] moreover — as the adhesives of an under coat — a starch-polyvinyl acetate graft copolymer — and — or in order to raise the water resisting property of an under coat in addition to the partial saponification object, an aqueous emulsion is used and a thing as specifically shown below is mentioned. An SBR latex, a polystyrene acrylic ester emulsion, a polyvinyl acetate emulsion, etc. are mentioned. When it combined with an SBR latex with many gel contents especially, the result good to the improvement in sensibility was shown in the waterproof improvement in a paint film, and coincidence. The under coat in this invention consists of a bulking agent and adhesives resin as a principal component, inorganic and the organic pigment which are used for the object for general paper manufacture and coating as a bulking agent are used for arbitration, and the following is specifically mentioned. For example, organic system resin impalpable powder, such as urea-formalin resin, styrene / methacrylic-acid copolymer, and polystyrene resin, etc. is in inorganic system impalpable powder, such as clay, a calcium carbonate, a magnesium carbonate, talc, a silica, the diatom earth, synthetic aluminum silicate, a zinc oxide, titanium oxide, an aluminum hydroxide, a barium sulfate, a calcium carbonate by which surface treatment was carried out, and a silica, and a list.

[0009] The rate of a compounding ratio of the bulking agent and binder of this undercoat is decided to be arbitration by the selected component, and, generally is between 20:1-1:1. Into an under coat, a thickener, fluorescent dye, a coloring color, a color pigment, a surfactant, an ultraviolet-rays inhibitor, a dispersant, a wax, an antioxidant, metallic soap, etc. can be blended in the range which does not spoil the effectiveness of this invention other than an above-mentioned bulking agent and a binder. In forming this undercoat, 1 - 15 g/m<sup>2</sup> (dry weight) of coverage is common, and although that coating is easily performed by applying to a paper base material using the usual coater, it is desirable to carry out coating by the coating method which can form a blade and the good coating layer of front-face nature called a slit die preferably.

[0010] Therefore, the sensible-heat coloring layer formed on an under coat is formed in a conventional method. If used for the electron-donative color-enhancing color and the common pressure sensitive paper which are used for this invention, a thermographic recording paper, etc., there will be especially no limit. The electron-donative color-enhancing color of white and light color can be used. Specifically for example, for example A 2 and 2 screw [4-(phtalide -3 and 6'-(N-cyclohexyl-N-methylamino)-3'-methyl SUPIRO [9'-xanthene]-2'-IRUAMIDO] phenyl] propane, 3-diethylamino-6-methyl-7-anilino-fluoran, 3-piperidino-6-methyl-7-anilino-fluoran, 3-(N-methyl-N-cyclohexylamino)-6-methyl-7-anilino-fluoran, 3-diethylamino-7-chloroanilino-fluorane, 3-[N-ethyl-N-(p-methylphenyl) amino]-6-methyl-7-anilino-fluoran, 3-diethylamino-7-(meta-trifluoromethyl) anilino-fluoran, 3-(N-ethyl-N-tetrahydrofurfuryl) amino-6-methyl-7-anilino-fluoran, It is the thing of fluoran system colors, such as 3-(N-ethyl-N-isopentyl) amino-6-methyl-7-anilino-fluoran and 3-dibutylamino-6-methyl-7-anilino-fluoran, which consists of 1 member at least.

[0011] The electronic receptiveness acid used for this invention is liquefied or evaporated above 70 degrees C, reacts with said color-enhancing color, and makes this color preferably beyond ordinary temperature. As electronic receptiveness acid, for example

4 and 4'-screw (p-toluenesulfonyl amino carbonylamino) diphenylmethane, A - isopropylidene diphenol, and 4 and 4', 4'-isopropylidene screw (2-chlorophenol), A - isopropylidene screw (2-methyl phenol), and 4 and 4', 4'-isopropylidene screw (2, 6-tert-butylphenol), -sec-butylidene diphenol, and 4 and 4', 4'-cyclohexylidene diphenol, 4-tert-butylphenol, 4-phenylphenol, 4-hydroxy diphenoxide, A naphthol, the beta-naphthol, methyl-4-hydroxy benzoate, A 4-hydroxy-acetophenone, a salicylic-acid anilide, a novolak mold phenol, A halogenation novolak mold phenol resin, 4, and 4'-thio screw (3-methyl-6-tert-butylphenol), P-hydroxybenzoic-acid propyl, P-hydroxybenzoic-acid isopropyl, P-hydroxybenzoic-acid butyl, P-hydroxybenzoic-acid benzyl, P-hydroxybenzoic-acid methylbenzyl, oxalic acid, a maleic acid, a tartaric acid, Aliphatic carboxylic acid, such as a citric acid, a succinic acid, and stearin acid, a benzoic acid, A p-tert-butyl benzoic acid, a phthalic acid, a gallic acid, a salicylic acid, 3-isopropyl salicylic acid, 3, a 5-G alpha-methylbenzyl salicylic acid, A screw (4-hydroxyphenyl) sulfide, 1, 7-JI (4-hydroxy phenylthio) -3, 5-dioxa heptane, With p-nitrobenzoic acid and these organic developer, for example, zinc, magnesium, A salt with polyvalent metal, such as aluminum, calcium, titanium, manganese, tin, and nickel, 4 and 4'-dihydroxy diphenylsulfone, 2, 4-dihydroxy diphenylsulfone, 3, 3'-dihydroxy diphenylsulfone, 3, the 3'-diamino -4, 4'-dihydroxy diphenylsulfone, 3, 3'-diaryl -4, 4'-dihydroxy-diphenylsulfone, 3, 3'-dichloro -4, 4'-dihydroxy diphenylsulfone, 4-hydroxy-diphenylsulfone, 4-hydroxy-4'-isopropyl diphenylsulfone, 4-hydroxy-4'-isopropoxy diphenylsulfone and 4-hydroxy-4'-benzyloxy diphenylsulfone, 2, 4-dihydroxy diphenylsulfone, 2, 4'-dihydroxy -4'-methyl diphenylsulfone, It is the thing which was chosen from 3, 4-dihydroxy phenyl-p-tris RUHON, the N-(o-toluoil)-p-toluene sulfo amide, the N-(p-tosyl)-N'-phenyl urea, etc. and which consists of 1 member at least.

[0012] the electronic receptiveness acid — usually — the color-enhancing color 1 weight section — receiving — 1 - 5 weight section — it is used, 1.5 - 3 weight section's coming out comparatively preferably, and mixing. moreover — this invention — the need — responding — the aromatic series ether and ester — and — or sensitizers, such as an aliphatic series amide or ureido, — For example, oxalic acid G p-methylbenzyl ester, oxalic acid G p-chloro benzyl ester, Dimethyl terephthalate ester, terephthalic-acid dibutyl ester, 4-ethoxy phenyl 4'-chloro benzyl ether, Terephthalic-acid dibenzyl ester, isophthalic acid dibutyl ester, 1-hydroxy naphthoic-acid phenyl ester, 1, 2-JI (3-methylphenoxy) ethane, 1, 2-JIFENOKISHI ethane, 1-phenoxy-2-(4-methylphenoxy) ethane, Diphenyl carbonate, diphenylsulfone, p-benzyl biphenyl, 2, and 2'-methylenebis (4-methyl-6-t-butylphenol), 4 and 4'-butylidenebis (6-t-butyl-3-methyl phenol), 1, 1, 3-tris (2-methyl-4-hydroxy-5-t-buthylphenyl) butane, 2 and 2'-methylenebis (4-ethyl-6-t-butylphenol), Hindered phenols, such as a 2, 4-G t-butyl-3-methyl phenol, 4, and 4'-thio screw (3-methyl-6-t-butylphenol), 2 -(2'-hydroxy-5'-methylphenyl)- Benzotriazol, a 2-hydroxy-4-benzyloxy benzophenone, etc. are mentioned.

[0013] it is mixed and used, and independence or in order to acquire sufficient heat responsibility, it is desirable still more desirable to carry out 3 weight sections use from 0.2 to the electron-donative color-enhancing color 1 weight section, and it boils, these heat fusibility matter, i.e., sensitizer, it receives, and is the 0.5 to 2.0 weight section. Distribution of these materials, an electron-donative color-enhancing color, the electronic receptiveness acid, and a sensitizer is performed with water soluble resin. Various wet grinding mills, such as a Sand grinder, attritor, a ball mill, and a Cobot mill, distribute each material as a dispersion-medium object using water with a surfactant besides water-soluble synthetic high polymers, such as polyacrylamide, a polyvinyl pyrrolidone, polyvinyl alcohol, a carboxymethyl cellulose, styrene maleic anhydride copolymer salts, and those derivatives, etc. In addition to both an electron-donative color-enhancing color, and electronic receptiveness both [ either or ], it distributes to coincidence, or depending on the case, an eutectic object may be created beforehand and a sensitizer may distribute.

[0014] In this invention, waxes, metallic soap, an ultraviolet ray absorbent, a shelf-life improver, fluorescent dye, etc. can be mentioned adhesives resin, inorganic or an organic pigment, and also if needed as an ingredient which otherwise constitutes a sensible-heat coloring layer.

[0015] The thing with the adhesives resin generally known as adhesives resin to combine is possible. As the example, polyvinyl alcohol, carboxy group denaturation polyvinyl alcohol, Aceto acetyl group denaturation polyvinyl alcohol, cation radical denaturation polyvinyl alcohol, Sulfone radical denaturation polyvinyl alcohol, silica denaturation polyvinyl alcohol, Starch and its derivative, gum arabic, gelatin, casein, methyl cellulose, Hydroxyethyl cellulose, a hydroxymethyl cellulose, a polyvinyl pyrrolidone, Polyacrylate, poly acrylamide, a styrene maleic anhydride copolymer, Water soluble resin, such as a methyl-vinyl-ether-maleic-anhydride copolymer and an isopropanal pyrene-maleic-anhydride copolymer, A styrene-butadiene latex, a vinyl acetate-acrylic ester copolymerization emulsion, Water-dispersion resin, such as a polyurethane emulsion, a polyvinyl chloride emulsion, a polyvinylidene chloride emulsion, a methacrylic ester copolymerization emulsion, and an emulsion of an acrylic ester copolymer, can be used. Moreover, in order to make the water resisting property of a paint film firm, it can use combining a cross linking agent.

[0016] As a cross linking agent, inorganic compounds, such as ammonium persulfate, and a ferric chloride, a magnesium chloride, or a boric acid, and a borax can be used for diglycidyl system compounds, such as polyamine system compounds, such as multiple-valued aldehyde system compounds, such as glyoxal, a glutaraldehyde, and dialdehyde starch, and polyethyleneimine, an epoxy system compound, polyamide resin, and glycerol diglycidyl ether, a dimethylol urea compound, and a list.

[0017] As a pigment, organic system resin impalpable powder, such as urea-formalin resin, styrene / methacrylic-acid copolymer, and polystyrene resin, can be raised to inorganic system impalpable powder, such as clay, a calcium carbonate, a magnesium carbonate, talc, a silica, the diatom earth, synthetic aluminum silicate, a zinc oxide, titanium oxide, an aluminum hydroxide, a barium sulfate, a calcium carbonate by which surface treatment was carried out, and a silica, and a list, for example.

[0018] As metallic soap, a higher-fatty-acid metal salt is used and zinc stearate, calcium stearate, aluminum stearate, etc. are mentioned. As a wax, paraffin wax, polyethylene wax, carnauba wax, a micro crystallin wax, Kandy Lynn Waxes, a montan wax, a fatty-acid amide system wax, etc. are mentioned.

[0019] A sensible-heat coloring layer coating is applied so that it may become 3 - 8 g/m<sup>2</sup> (desiccation) on one front face of a sheet-like base material, and a heat-sensitive recording layer is formed of it. In the protective layer prepared on a sensible-heat coloring layer, a dry pick can be pressed down without the weight ratio after drying 98% or more of polyvinyl alcohol affecting impression of shelf life and printing ink 1500 or more degrees of polymerization and whenever [ saponification ], by [ of the whole protective layer ] containing 20 to 50% of the weight. The combination fewer than 20 % of the weight of coat formation of a protective layer is inadequate, and shelf life falls by it. Moreover, when blended more mostly than 50 % of the weight, the width of face of the printing conditions at the time of offset printing became narrow, printed, and became that of \*\* potatoes. It will be in the condition that this has the narrow water width as used in the field of the printing industry, and if the dampening water amount of supply is made [ many ] in order to suppress the printing greasing of the non-streak section at the time of printing, the poor repeatability of the concentration nonuniformity of the image section or a halftone dot configuration will become easy to generate easily, and the water defeat phenomenon in emulsification ink will happen. if the dampening water amount of supply must be lessened slightly for this reason, but lessening the dampening water amount of supply slightly, and operating the offset press

requires skill and it lessens it too much — generating of a greasing — when many [ too ], there was generating of water defeat, and it printed very much and changed into the \*\*\*\*\* condition. In the range which does not check the effectiveness of this invention 1500 or more degrees of polymerization and whenever [ saponification ] as adhesives resin in a protective layer other than 98% or more of polyvinyl alcohol, aceto acetylation polyvinyl alcohol, Denaturation polyvinyl alcohol, such as carboxyl denaturation polyvinyl alcohol, Starch, casein, gelatin, glue, a polyamide, polyacrylamide, It can blend combining hydroxyethyl cellulose, methyl cellulose, a cull BOKIME chill cellulose, a hydronalium KIPURO pill cellulose, a styrene maleic anhydride copolymer salt, a diisobutylene-maleic-anhydride copolymer salt, etc.

[0020] Inorganic pigments, such as a calcium carbonate, clay, a baking kaolin, talc, titanium oxide, a magnesium carbonate, a zinc oxide, an aluminum silicate, a calcium silicate, a silica, and an aluminum hydroxide, a starch grain child, wheat flour, silicon resin, a urea and formalin resin, phenol resin, melamine formalin resin, an epoxy resin, guanamine formalin resin, polystyrene resin, etc. can be used together as a pigment. Moreover, according to the approach of this invention, a protective layer can improve a water resisting property further especially for the application of which an advanced water resisting property is required by using together cross linking agents, such as a melamine, epoxy, an aziridine, glyoxal, dimethylol urea, the poly aldehyde, a boric acid, a borax, and a zirconium salt, for example, although sufficient water resisting property can be given.

[0021] Into a protective layer, the wax and metallic soap which were illustrated below if needed can be blended. A higher-fatty-acid amide, for example, octadecanamide, besides paraffin wax, a cull navarho wax, a micro crystallin wax, and polyethylene wax, ethylene bis-octadecanamide, higher-fatty-acid ester, higher-fatty-acid polyvalent metallic salt, i.e., zinc stearate, aluminum stearate, calcium stearate, zinc oleate, etc. are mentioned. Putting in various additives, such as an oil repellent agent, a defoaming agent, a viscosity modifier, a surfactant, fluorescent dye, an ultraviolet ray absorbent, a coloring color, and a color pigment, in the range which otherwise does not spoil the effectiveness of this invention does not interfere.

[0022] a protective layer — dry weight — it is — 0.1 - 6 g/m<sup>2</sup> — 0.5-4 g/m<sup>2</sup> coating is carried out more preferably. In less than two 0.1 g/m, if it is deficient in the effectiveness as a protective layer and 6 g/m<sup>2</sup> is exceeded, it will become the cause that coloring sensibility falls. Moreover, a protective layer can also be made into the multilayer more than two-layer.

[0023] There is no limitation according to rank in the base material ingredient used for this invention, for example, it can use suitably paper of fine quality, a report grade paper, coat paper, art paper, cast coated paper, a resin laminated paper, a polyolefine system synthetic paper, a synthetic fiber paper, a synthetic-resin film, etc. for it. As an approach of forming a sensible-heat coloring layer, any of the known methods of application, such as the Ayr knife method, the blade method, the gravure method, the roll coater method, a spray method, a dip method, the bar method, and the extrusion method, may be used. Moreover, although the same coating method as the approach of forming a sensible-heat coloring layer as an approach of forming a protective layer is held, they are the Ayr knife method, the gravure method, the roll coater method, and a spray method.. The approach of writing lightly the protective layer coating which carried on a sensible-heat coloring layer like a dip method and the extrusion method is desirable. Osmosis of the oil from a rear face or a plasticizer can be suppressed, or a back layer can also be prepared for curl control.

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## EXAMPLE

[Example] An example explains this invention still more concretely below.

Preparation of the formation (1) pigment dispersion liquid of example 1 under coat Amount (% of the weight)

Baking clay 30 (en gel heart company make, trade name ANSI REXX 93)

47 % of the weight liquid of polystyrene particles 25 (the Mitsui Toatsu Chemicals, Inc. make, trade name gross DERU104s)

20 % of the weight liquid of starch-vinyl acetate graft copolymerization resin 38 (Japanese dregs chemistry company make, trade name PETOKOTO c8)

Carboxymethyl cellulose 0.5 (the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, trade name AG gum)

40 % of the weight liquid of sodium polyacrylate 0.3 (the Kao Corp. make, trade name poise 520)

Defoaming agent 0.02 (the Sannopuko make, a trade name DF 122)

After the homogenizer distributed for 5 minutes, it blended 6 % of the weight (the Asahi Chemical Co., Ltd. make, trade name L1537) of 50 % of the weight liquid of SBR latexes, and considered as the coating for under coats. 8 g/m<sup>2</sup> (desiccation) coating of this coating liquid was carried out in the high-quality paper of basis-weight 40 g/m<sup>2</sup> by the chip blade method, and the under coat was formed.

[0025]

Formation of a sensible-heat layer (1) Preparation of color-enhancing color dispersion liquid A Component Amount (% of the weight)

3-dibutylamino-6-methyl-7-ANIRINO 40 Fluoran Polyvinyl alcohol 10% liquid 40 (polymerization degree 500, whenever [ saponification ] 90%)

Water 20 (2) Preparation of development nature compound dispersion liquid B Component Amount (% of the weight)

4 and 4'-dihydroxy diphenylsulfone 40 Polyvinyl alcohol 10% liquid 40 (polymerization degree 500, whenever [ saponification ] 90%)

Water 20 [0026]

(3) Preparation of sensitizer dispersion liquid C Component Amount (% of the weight)

Oxalic acid G p-methylbenzyl ester 40 Polyvinyl alcohol 10% liquid 40 (polymerization degree 500, whenever [ saponification ] 90%)

Water 20 (4) Preparation of shelf-life improver dispersion liquid D Component Amount (% of the weight)

4-(2-methyl-glycidyoxy)-4'- 40 Benzyloxy diphenylsulfone Polyvinyl alcohol 10% liquid 40 (polymerization degree 500, whenever [ saponification ] 90%)

water 20 — these constituents were separately distributed in the vertical mold sand mill (the product made from eye MEKKUSU, Sand grinder).

(5) Preparation of pigment dispersion liquid E Component Amount (% of the weight)

Precipitated calcium carbonate 40 (the product made from \*\* Co. in Shiroishi, brilliant 15)

0.7% solution of sodium hexametaphosphate 60 — this constituent was distributed by the cow loess disperser.

[0027] Furthermore, it is 10% starch-vinyl acetate graft copolymerization resin as 20% octadecanamide distribution object and adhesives H as distributed object F liquid as 49% of styrene butadiene latex (the Sumitomo Dow-Jones company make, trade name P0Y72), and adhesives I as 20% zinc stearate distribution object and distributed object G liquid. (Japanese dregs chemistry company make, trade name PETOKOTO c8) It prepared. Using these distributed objects and adhesives, the weight ratio after desiccation blended so that it might be set to A:B:C:D:E:F:G:H:I=10:20:20:3:22:5:5:1 0:5, and it considered as coating liquid. 6 g/m<sup>2</sup> (desiccation) coating of this coating liquid was carried out on the above-mentioned under coat by the rod blade method, and the sensible-heat coloring layer was formed.

[0028] As the formation adhesives resin (A, B) of a protective layer whenever [ a degree of polymerization 1700 and / saponification ] — 99.5% polyvinyl alcohol (Kuraray Make —) Trade name OTP4H, acrylic emulsion resin (the Mitsui Toatsu Chemicals make, trade name barrier star B1850), As a pigment (C), fines silicic acid (the product made from the Mizusawa chemistry, trade name Ms. KASHIRU P603), Protective layer coating liquid is prepared so that a dry weight ratio may be set to A:B:C:D=40:10:40:10 using zinc stearate (D) 20 more%. After 2 g/m<sup>2</sup> (desiccation) spreading and desiccation, 5 - 8% of moisture, and linear pressure 80 kg/cm performed the calendering with the rod blade on the sensible-heat coloring layer of the sensible-heat coloring paper which formed this previously, and the thermal recording ingredient was created.

[0029] Example of a comparison Except having made 38 % of the weight (Japanese dregs chemistry company make, trade name PETOKOTO c8) of 20 % of the weight solutions of starch-vinyl acetate graft copolymerization resin of the under coat in one example 1 into 18 % of the weight, and having made baking clay (en gel heart company make, trade name ANSI REXX 93) into 55 % of the weight, same processing was performed and the thermal recording ingredient was created.

[0030] Example of a comparison The degree of polymerization 1700 of the protective layer in two examples 1, whenever [ saponification ] 99.5% Except having made 40 % of the weight (Kuraray Make, trade name OTP4H) of polyvinyl alcohol into 15 % of the weight, and having made fines silicic acid (the product made from the Mizusawa chemistry, trade name Ms. KASHIRU P603) into 65 % of the weight from 40 % of the weight, same processing was performed and the thermal recording ingredient was created.

[0031] Example of a comparison Except having combined the same protective layer as the same under coat as the example 1 of 3 comparisons, and the example 2 of a comparison, the same processing as an example 1 was performed, and the thermal recording ingredient was created.

[0032]

[Table 1]

	感 度	耐ホリ塩化ビニルラッ 7°性（保存率％）	印刷水負け 評価	トライビツクの 評価
実施例 1	1. 3 3	9 8	○	○
比較例 1	1. 3 2	9 3	○	×
比較例 2	1. 1 1	6 5	×	○
比較例 3	1. 1 5	6 1	×	×

[0033] as the adhesives resin of a protective layer — whenever [ 1000 or more degrees of polymerization and / saponification ] — 98% or more of polyvinyl alcohol — as 20 to 50 weight section implication, and the adhesives resin of an under coat — water soluble resin — a starch-polyvinyl acetate graft copolymer — and — or by carrying out 30 weight sections content of the partial saponification object from 10, shelf life was good at high sensitivity, and the good thing of offset-printing fitness with picking-proof nature was obtained.

[0034] Sensitometry : system sensible-heat facsimile was measured using what was converted into the trial. Pulse width was modulated on 10ms/line of one-line chart lasting time, and the conditions of 8\*8 dots/mm of scanning density, the impression energy per dot was adjusted to 0.5ms, and printing of 64 lines was performed. The coloring concentration in that case was measured by Macbeth concentration meter RD-514, and it considered as the value representing record sensibility.

[0035] Polyvinyl chloride-proof lap nature : The printing object which evaluated record sensibility was stuck on the polyvinyl chloride wrap film, it covered with the polyvinyl chloride wrap film from on the further, and the printing concentration after one-week progress was measured at 40 degrees C Macbeth concentration meter RD-514. The rate of preservation was computed from change of printing concentration, and extent of polyvinyl chloride-proof lap nature was evaluated.

[0036] Printing water defeat trial : After ink's having added 0.5 cc of water to ink 0.25g with \*\*\*\* coloring matter best KYUA RNC-red (tuck 6) using the \*\*\*\*\* RI circuit tester, scouring ink and water for 1 minute with the ink kneading roller and making ink emulsify, it evaluated by performing a printing trial.

O x which ink transferred to paper good Transition of ink was not appropriate. [0037] Dry pick trial : Using a \*\*\*\*\* RI circuit tester, ink adds ink 0.25g with \*\*\*\* coloring matter best KYUA RNC-red (tuck 15), and scours ink and water for 1 minute with an ink kneading roller. The printing trial was performed after making ink emulsify.

O x in which a paint film did not exfoliate at the time of printing A paint film did not exfoliate at the time of printing.

[Translation done.]



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(54) 【発明の名称】 感熱記録材料

(57) 【要約】

【目的】 高感度で保存性が良く、耐ピッキング性のあるオフセット印刷適性の良好な感熱記録材料を製造する。

【構成】 シート状支持体上に有機及び又は無機顔料と接着剤樹脂を含む下塗り層を設けその上に無色ないし淡色の電子供与性発色性染料、加熱により該発色性染料を発色させる電子受容性顕色性化合物、及び接着剤樹脂を主成分として含有する感熱発色層及び保護層を設けた感熱記録紙において、前記保護層が重合度 1000 以上、鹸化度 98% 以上のポリビニルアルコールを乾燥後の重量比率が保護層全体の 20~50 重量% 含有し、かつ前記下塗り層が接着剤樹脂として澱粉-ポリ酢酸ビニルグラフト共重合体及び又はその部分鹸化物を乾燥後の重量比率が下塗り層全体の 10~30 重量% 含有することを特徴とする感熱記録材料。

## 【特許請求の範囲】

【請求項 1】 シート状支持体上に有機及び又は無機顔料と接着剤樹脂を含む下塗り層を設けその上に無色ないし淡色の電子供与性発色性染料、加熱により該発色性染料を発色させる電子受容性顕色性化合物、及び接着剤樹脂を主成分として含有する感熱発色層及び保護層を設けた感熱記録紙において、前記保護層が重合度 1000 以上、鹼化度 98% 以上のポリビニルアルコールを乾燥後の重量比率が保護層全体の 20~50 重量% 含有し、かつ前記下塗り層が接着剤樹脂として澱粉-ポリ酢酸ビニルグラフト共重合体及び又はその部分鹼化物を乾燥後の重量比率が下塗り層全体の 10~30 重量% 含有することを特徴とする感熱記録材料。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、感熱記録材料に関する。更に詳しくは高感度で保存性が良く、耐ピックアップ性のあるオフセット印刷適性を有する感熱記録材料に関するものである。

## 【0002】

【従来の技術】 感熱記録材料は一般に紙、合成紙、またはプラスチックフィルムなどからなるシート状支持体上に、電子供与性ロイコ染料のような発色性染料と、電子受容性のフェノール性化合物などのような顕色性化合物と、接着剤樹脂とを主成分として含む感熱発色層を設けたものであって、これら発色性染料と顕色剤とを熱エネルギーによって反応させて発色記録画像を得ることができる。一方、感熱記録方式は単に加熱するだけで発色画像が得られ、またこの記録装置を比較的簡単にコンパクトなものにすることができるなどの利点が高く評価され、ファクシミリや自動券売機、科学計測器、CD/ATM、POS ラベル用プリンターなど各種情報記録方式として広範囲に利用されている。

【0003】 このような用途の広がりと共に、高い保存性に加えて、印刷性を要求されてきている。高い保存性を得るために、感熱層上に保護層を設けることが一般的に行われている（特公昭 44-27880 号公報、特開昭 48-51644 号公報）。しかし、このような保護層を感熱層上に設けると、サーマルヘッドからの感熱層への熱の伝導が保護層を通過して到達するため、感度低下を避けることが出来ない。そこで、この感度低下を防ぐため、熱伝導率の低い支持体にすることが考えられる（特開昭 55-164192 号公報）。すなわち、下塗り層を設け、且つこの下塗り層を空隙の多い層としている。このようなポーラスな下塗り層を有する層構成の感熱記録紙へ印刷した場合、ピックアップに対して弱くなってしまう。

## 【0004】

【発明が解決しようとする課題】 本発明は、感熱記録材料に関する。更に詳しくは高感度で保存性が良く、耐ピックアップ性のあるオフセット印刷適性を有する感熱記録

材料を提供することにある。

## 【0005】

【課題を解決するための手段】 本発明の目的は、シート状支持体上に有機及び又は無機顔料と接着剤樹脂を含む下塗り層を設けその上に無色ないし淡色の電子供与性発色性染料、加熱により該発色性染料を発色させる電子受容性顕色性化合物、及び接着剤樹脂を主成分として含有する感熱発色層及び保護層を設けた感熱記録紙において、前記保護層が重合度 1000 以上、鹼化度 98% 以上のポリビニルアルコールを乾燥後の重量比率が保護層全体の 20~50 重量% 含有し、かつ前記下塗り層が接着剤樹脂として澱粉-ポリ酢酸ビニルグラフト共重合体及び又はその部分鹼化物を乾燥後の重量比率が下塗り層全体の 10~30 重量% 含有することを特徴とする感熱記録材料によって達成された。

【0006】 保護層中に重合度 1500 以上、鹼化度 98% 以上のポリビニルアルコールを乾燥後の重量比率が保護層全体の 20 重量% 以上含むことによって保存性は飛躍的に向上するが、保護層の皮膜形成能が向上した結果、印刷時のピックアップが悪化した。これについて対策を検討するため、下塗り層の接着剤樹脂として塗膜形成時にポーラスな層形成の出来き、且つ接着強度向上が図れる接着剤樹脂を選択した。その結果、澱粉-ポリ酢酸ビニルグラフト共重合体及び又はその部分鹼化物を乾燥後の重量比率が下塗り層全体の 10~30 重量% の範囲で含有することによって感度の低下を起さずに印刷時のピックアップが解決できることを見出した。しかし、澱粉-ポリ酢酸ビニルグラフト共重合体及び又はその部分鹼化物が乾燥後の重量比率が下塗り層全体の 10 重量% 未満では下塗り層の塗膜強度が不十分で印刷時にピックアップが発生した。しかし澱粉-ポリ酢酸ビニルグラフト共重合体及び又はその部分鹼化物を乾燥後の重量比率が下塗り層全体の 30 重量% より多く配合すると感度が低下した。本発明によって得られる感熱記録紙は従来無かった保存性、感度に優れ又印刷時のピックアップの良好な品質を有する記録材料とすることが出来た。

【0007】 本発明における澱粉-ポリ酢酸ビニルグラフト共重合体及び又はその鹼化物とは天然澱粉、天然澱粉含有物、分画されたアミロース、及びアミロペクチン、及びそれらのエーテル化澱粉、エステル化澱粉、架橋澱粉、グラフト変成澱粉、酸化澱粉、デキストリン澱粉、酸処理澱粉、酵素変成澱粉より選ばれた 1 種以上の変性を受けた化工澱粉に酢酸ビニルあるいはその他のビニルエステル類をさせたもの及び又はグラフトした酢酸ビニル部分が鹼化したものを含む。

【0008】 又、下塗り層の接着剤として澱粉-ポリ酢酸ビニルグラフト共重合体及び又はその部分鹼化物以外に下塗り層の耐水性を向上させるため、水性エマルジョンが用いられ、具体的には例えば以下に示すようなものが挙げられる。SBR ラテックス、ポリスチレン-アクリル

リル酸エステルエマルジョン、ポリ酢酸ビニルエマルジョン等が挙げられる。中でもゲル含量の多いSBRラテックスと組み合わせた時、塗膜の耐水性向上と同時に感度向上に良好な結果を示した。本発明における下塗り層は主成分として充填剤と接着剤樹脂とからなり、充填剤としては一般製紙用、塗工用に用いられる無機、有機の顔料が任意に用いられ、具体的には以下のようなものが挙げられる。例えば、クレー、炭酸カルシウム、炭酸マグネシウム、タルク、シリカ、ケイソウ土、合成ケイ酸アルミニウム、酸化亜鉛、酸化チタン、水酸化アルミニウム、硫酸バリウム、表面処理された炭酸カルシウムやシリカなどの無機系微粉末、並びに、尿素-ホルマリン樹脂、スチレン/メタクリル酸共重合体、ポリスチレン樹脂等の有機系樹脂微粉末等がある。

【0009】この下塗り層の充填剤と結合剤の配合比率は選択した成分によって任意に決められ一般的には20:1~1:1の間である。下塗り層中には上述の充填剤、結合剤以外に本発明の効果を損なわない範囲で増粘剤、蛍光染料、着色染料、着色顔料、界面活性剤、紫外線防止剤、分散剤、ワックス、酸化防止剤、金属石鹸等を配合することが出来る。この下塗り層を形成するに当たっては塗布量は1~15 g/m<sup>2</sup> (乾燥重量) が一般的でありその塗工は通常の塗工機を用いて紙支持体に塗布することによって容易に行なわれるが、好ましくはブレードやスリットダイといった表面性の良い塗工層を形成できる塗工方式で塗工することが好ましい。

【0010】下塗り層上に形成する感熱発色層は常法に拠って形成する。本発明に用いられる電子供与性発色性染料、一般の感圧記録紙、感熱記録紙等に用いられているものであれば特に制限はない。例えば白色、淡色の電子供与性発色性染料が使用でき、具体的には例えば、2, 2ビス〔4-〔6'- (N-シクロヘキシル-N-メチルアミノ) -3'-メチルスピロ〔フタリド-3, 9'-キサンテン〕-2'-イラムイド〕フェニル〕プロパン、3-ジエチルアミノ-6-メチル-7-アニリノフルオラン、3-ピペリジノ-6-メチル-7-アニリノフルオラン、3-(N-メチル-N-シクロヘキシルアミノ)-6-メチル-7-アニリノフルオラン、3-ジエチルアミノ-7-クロロアニリノフルオラン、3-〔N-エチル-N-(p-メチルフェニル)アミノ〕-6-メチル-7-アニリノフルオラン、3-ジエチルアミノ-7-(メタトリフルオロメチル)アニリノフルオラン、3-(N-エチル-N-テトラヒドロフルフリル)アミノ-6-メチル-7-アニリノフルオラン、3-(N-エチル-N-イソペンチル)アミノ-6-メチル-7-アニリノフルオラン、3-ジブチルアミノ-6-メチル-7-アニリノフルオラン等のフルオラン系染料の少なくとも1員からなるものである。

【0011】本発明に用いられる電子受容性酸性物質は、常温以上、好ましくは70℃以上で液化または気化

して前記発色性染料と反応してこれを発色させるものである。電子受容性酸性物質としては、例えば4, 4'-ビス(p-トルエンスルホニルアミノカルボニルアミノ)ジフェニルメタン、4, 4'-イソプロピリデンジフェノール、4, 4'-イソプロピリデンビス(2-クロロフェノール)、4, 4'-イソプロピリデンビス(2-メチルフェノール)、4, 4'-イソプロピリデンビス(2, 6-tert-ブチルフェノール)、4, 4'-sec-ブチリデンジフェノール、4, 4'-シクロヘキシリデンジフェノール、4-tert-ブチルフェノール、4-フェニルフェノール、4-ヒドロキシジフェノキシド、ナフトール、β-ナフトール、メチル-4-ヒドロキシベンゾエート、4-ヒドロキシアセトフェノン、サリチル酸アニリド、ノボラック型フェノール、ハロゲン化ノボラック型フェノール樹脂、4, 4'-チオビス(3-メチル-6-tert-ブチルフェノール)、p-ヒドロキシ安息香酸プロピル、p-ヒドロキシ安息香酸イソプロピル、p-ヒドロキシ安息香酸ブチル、p-ヒドロキシ安息香酸ベンジル、p-ヒドロキシ安息香酸メチルベンジル、シュウ酸、マレイン酸、酒石酸、クエン酸、コハク酸、ステアリン酸などの脂肪族カルボン酸、安息香酸、p-tert-ブチル安息香酸、フタル酸、没食子酸、サリチル酸、3-イソプロピルサリチル酸、3, 5-ジ-α-メチルベンジルサリチル酸、ビス(4-ヒドロキシフェニル)スルフィド、1, 7-ジ(4-ヒドロキシフェニルチオ)-3, 5-ジオキサヘプタン、p-ニトロ安息香酸、これら有機顔色剤と例えば亜鉛、マグネシウム、アルミニウム、カルシウム、チタン、マンガン、錫、ニッケル等の多価金属との塩、4, 4'-ジヒドロキシジフェニルスルホン、2, 4-ジヒドロキシジフェニルスルホン、3, 3'-ジヒドロキシジフェニルスルホン、3, 3'-ジアミノ-4, 4'-ジヒドロキシジフェニルスルホン、3, 3'-ジアリル-4, 4'-ジヒドロキシジフェニルスルホン、3, 3'-ジクロロ-4, 4'-ジヒドロキシジフェニルスルホン、4-ヒドロキシジフェニルスルホン、4-ヒドロキシ-4'-イソプロピルジフェニルスルホン、4-ヒドロキシ-4'-イソプロピルオキシジフェニルスルホン、4-ヒドロキシ-4'-ベンジルオキシジフェニルスルホン、2, 4-ジヒドロキシジフェニルスルホン、2, 4'-ジヒドロキシ-4'-メチルジフェニルスルホン、3, 4-ジヒドロキシフェニル-p-トリルスルホン、N-(o-トルオイル)-p-トルエンスルホアミド、N-(p-トルエンスルホニル)-N'-フェニル尿素などから選ばれた少なくとも1員からなるものである。

【0012】電子受容性酸性物質は通常、発色性染料1重量部に対し1~5重量部、好ましくは1.5~3重量部の割合で混合して使用される。又、本発明では必要に応じて芳香族エーテル、エステル及び又は脂肪族アミド

又はウレイド等の増感剤、例えばシュウ酸ジ-p-メチルベンジルエステル、シュウ酸ジ-p-クロロベンジルエステル、テレフタル酸ジメチルエステル、テレフタル酸ジブチルエステル、4-エトキシフェニル-4'-クロロベンジルーエーテル、テレフタル酸ジベンジルエステル、イソフタル酸ジブチルエステル、1-ヒドロキシナフトエ酸フェニルエステル、1, 2-ジ(3-メチルフェノキシ)エタン、1, 2-ジフェノキシエタン、1-フェノキシ-2-(4-メチルフェノキシ)エタン、炭酸ジフェニル、ジフェニルスルホン、p-ベンジルピフェニル、2, 2'-メチレンビス(4-メチル-6-t-ブチルフェノール)、4, 4'-ブチリデンビス(6-t-ブチル-3-メチルフェノール)、1, 1, 3-トリス(2-メチル-4-ヒドロキシ-5-t-ブチルフェニル)ブタン、2, 2'-メチレンビス(4-エチル-6-t-ブチルフェノール)、2, 4-ジ-t-ブチル-3-メチルフェノール、4, 4'-チオビス(3-メチル-6-t-ブチルフェノール)等のヒンダードフェノール類、2-(2'-ヒドロキシ-5'-メチルフェニル)-ベンゾトリアゾール、および2-ヒドロキシ-4-ベンジルオキシベンゾフェノン等が挙げられる。

【0013】これらの熱可融性物質すなわち増感剤は単独、あるいは混合して用いられ、充分な熱応答性を得るためには、電子供与性発色性染料1重量部に対して0.2から3重量部使用することが望ましく、更に好ましくはに対して0.5から2.0重量部である。これらの素材、電子供与性発色性染料、電子受容性酸性物質、増感剤の分散は水溶性樹脂と共に行われる。それぞれの素材を水を分散媒体として使用しサンドグラインダー、アトライター、ボールミル、コボーミル等の各種湿式粉碎機によってポリアクリルアミド、ポリビニルピロリドン、ポリビニルアルコール、カルボキシメチルセルロース、およびスチレン-無水マレイン酸共重合体塩及びそれらの誘導体などのような水溶性合成高分子化合物の他、界面活性剤などと共に分散する。増感剤は電子供与性発色性染料、電子受容性酸性物質のいずれかまたは両方に加え、同時に分散するか、場合によっては予め共融物を作成し、分散しても良い。

【0014】本発明において、他に感熱発色層を構成する材料としては接着剤樹脂、無機または有機顔料、更に必要に応じワックス類、金属石鹸、紫外線吸収剤、保存性向上剤、蛍光染料などを挙げることができる。

【0015】接着剤樹脂としては一般に知られている接着剤樹脂との組み合わせることは可能である。その例としては、ポリビニルアルコール、カルボキシ基変性ポリビニルアルコール、アセトアセチル基変性ポリビニルアルコール、カチオン基変性ポリビニルアルコール、スルホン基変性ポリビニルアルコール、シリカ変性ポリビニルアルコール、澱粉及びその誘導体、アラビアゴ

ム、ゼラチン、カゼイン、メチルセルロース、ヒドロキシエチルセルロース、ヒドロキシメチルセルロース、ポリビニルピロリドン、ポリアクリル酸塩、ポリアクリルアミド、スチレン-無水マレイン酸共重合体、メチルビニルーエーテル-無水マレイン酸共重合体、イソプロピレン-無水マレイン酸共重合体等の水溶性樹脂、スチレン-ブタジエンラテックス、酢酸ビニルーアクリル酸エステル共重合エマルジョン、ポリウレタンエマルジョン、ポリ塩化ビニルエマルジョン、ポリ塩化ビニリデンエマルジョン、メタクリル酸エステル共重合エマルジョンおよびアクリル酸エステル共重合体のエマルジョン等の水分散性樹脂が使用できる。又、塗膜の耐水性を強固なものとするためには、架橋剤とを組み合わせる用いることができる。

【0016】架橋剤としては、グリオキサール、グルタルアルデヒド、ジアルデヒドスターチ等の多価アルデヒド系化合物、ポリエチレンイミン等のポリアミン系化合物、エポキシ系化合物、ポリアミド樹脂、グリセリンジグリシルーエーテル等のジグリシルー系化合物、ジメチロールウレア化合物、並びに過硫酸アンモニウムや塩化第二鉄、および塩化マグネシウム等のような無機化合物またはホウ酸、ホウ砂を用いることができる。

【0017】顔料としては、例えば、クレール、炭酸カルシウム、炭酸マグネシウム、タルク、シリカ、ケイソウ土、合成ケイ酸アルミニウム、酸化亜鉛、酸化チタン、水酸化アルミニウム、硫酸バリウム、表面処理された炭酸カルシウムやシリカなどの無機系微粉末、並びに、尿素-ホルマリン樹脂、スチレン/メタクリル酸共重合体、ポリスチレン樹脂等の有機系樹脂微粉末をあげることができる。

【0018】金属石鹸としては、高級脂肪酸金属塩が用いられ、ステアリン酸亜鉛、ステアリン酸カルシウム、ステアリン酸アルミニウム等が挙げられる。ワックスとしては、パラフィンワックス、ポリエチレンワックス、カルナバワックス、マイクロクリスタリンワックス、キャンデリンワックス、モンタンワックス、脂肪酸アミド系ワックス等が挙げられる。

【0019】感熱発色層塗料はシート状支持体の一表面に3~8g/m<sup>2</sup>(乾燥)となる様に塗布され、それによって感熱記録層が形成される。感熱発色層上に設けられる保護層には、重合度1500以上、鹼化度98%以上のポリビニルアルコールを乾燥後の重量比率が保護層全体の20~50重量%含むことによって保存性と印刷インキの着肉に影響を与えないでドライピックを抑えられる。20重量%より少ない配合では、保護層の皮膜形成が不十分で保存性が低下する。また50重量%より多く配合するとオフセット印刷時の印刷条件の幅が狭くなり印刷しづらいものとなった。これは印刷業界でいわれる水幅が狭いという状態であり、印刷時非画線部の印刷地汚れを抑える為に湿し水供給量を多くすると、乳化イ

ンキによる水負け現象が容易に発生し易くなってしまう、画像部の濃度ムラや網点形状の再現性不良が起こるというものである。この為、湿し水供給量を少なめにせざるをえないが、湿し水供給量を少なめにして、オフセット印刷機を運転することは熟練を要し、少なくし過ぎると地汚れの発生、多過ぎると水負けの発生があり、非常に印刷しづらい状態となった。保護層中の接着剤樹脂として重合度1500以上、鹸化度98%以上のポリビニルアルコール以外に本発明の効果を阻害しない範囲でアセトアセチル化ポリビニルアルコール、カルボキシル変性ポリビニルアルコールなどの変性ポリビニルアルコール、デンプン、カゼイン、ゼラチン、にかわ、ポリアミド、ポリアクリルアミド、ヒドロキシエチルセルロース、メチルセルロース、カルボキメチルセルロース、ヒドロキシプロピルセルロース、スチレン-無水マレイン酸共重合体塩、ジイソブチレン-無水マレイン酸共重合体塩などを組み合わせて配合することが出来る。

【0020】顔料として例えば、炭酸カルシウム、クレ-、焼成カオリン、タルク、酸化チタン、炭酸マグネシウム、酸化亜鉛、ケイ酸アルミニウム、ケイ酸カルシウム、シリカ、水酸化アルミニウムなどの無機顔料、でんぷん粒子、小麦粉、シリコン樹脂、尿素・ホルマリン樹脂、フェノール樹脂、メラミン・ホルマリン樹脂、エポキシ樹脂、グアナミン・ホルマリン樹脂、ポリスチレン樹脂などが併用することが出来る。又、本発明の方法によれば保護層は十分な耐水性を付与することができるが、特に高度な耐水性を要求される用途では、例えばメラミン、エポキシ、アジリジン、グリオキサール、ジメチロールウレア、ポリアルデヒド、ホウ酸、ホウ砂、ジルコニウム塩などの架橋剤を併用することによって更に耐水性を向上することが出来る。

【0021】保護層中には必要に応じて以下に例示したワックス、金属石鹸を配合することができる。パラフィンワックス、カルナバロウワックス、マイクロクリスタ

#### 下塗り層の形成

##### (1) 顔料分散液の調製

焼成クレ-

量 (重量%)

3 0

(エンゲルハート社製、商品名アンシレックス93)

ポリスチレン粒子47重量%液

2 5

(三井東圧社製、商品名グロスデール104s)

澱粉-酢酸ビニルグラフト共重合樹脂20重量%液

3 8

(日澱化学社製、商品名ベトコートc8)

カルボキシメチルセルロース

0 . 5

(第一工業製薬社製、商品名AGガム)

ポリアクリル酸ソーダ40重量%液

0 . 3

(花王社製、商品名ボイズ520)

消泡剤

0 . 0 2

(サンノブコ社製、商品名DF122)

を5分間ホモジナイザーで分散した後、SBRラテックス50重量%液(旭化成社製、商品名L1537)6重

リンワックス、ポリエチレンワックスの他、高級脂肪酸アミド例えばステアリン酸アミド、エチレンビスステアリン酸アミド、高級脂肪酸エステル、高級脂肪酸多価金属塩すなわちステアリン酸亜鉛、ステアリン酸アルミニウム、ステアリン酸カルシウム、オレイン酸亜鉛などが挙げられる。他に本発明の効果を損なわない範囲で撥油剤、消泡剤、粘度調節剤、界面活性剤、蛍光染料、紫外線吸収剤、着色染料、着色顔料等各種添加剤をいれることはさしつかえない。

【0022】保護層は、乾燥重量で、0.1~6g/m<sup>2</sup>、より好ましくは0.5~4g/m<sup>2</sup>塗工される。0.1g/m<sup>2</sup>未満では保護層としての効果に乏しく、6g/m<sup>2</sup>を越えると発色感度が低下する原因となる。又保護層は2層以上の多層にすることもできる。

【0023】本発明に用いられる支持体材料には、格別の限定はなく、例えば上質紙、中質紙、コート紙、アート紙、キャストコート紙、樹脂ラミネート紙、ポリオレフィン系合成紙、合成繊維紙、合成樹脂フィルム等を適宜使用することが出来る。感熱発色層を形成する方法としてはエア-ナイフ法、ブレード法、グラビア法、ロールコーター法、スプレー法、ディップ法、バー法、およびエクストルージョン法などの既知の塗布方法のいずれを利用しても良い。又、保護層を形成する方法としては感熱発色層を形成する方法と同様の塗工方式が挙げられるが、エア-ナイフ法・グラビア法・ロールコーター法・スプレー法・ディップ法およびエクストルージョン法のような感熱発色層上にのせた保護層塗料を軽くかきとる方法が好ましい。裏面からの油や可塑剤の浸透を抑えたり、カールコントロールのためにバック層を設けることもできる。

##### 【0024】

【実施例】以下に本発明を実施例によってさらに具体的に説明する。

##### 実施例1

量%配合し下塗り層用塗料とした。この塗工液をチップブレード法によって坪量40g/m<sup>2</sup>の上質紙上に8g

／m<sup>2</sup>（乾燥）塗工し、下塗り層を形成した。

【0025】

#### 感熱層の形成

##### (1) 発色性染料分散液 A の調製

成分	量（重量％）
3-ジブチルアミノ-6-メチル-7-アニリノフルオラン	40
ポリビニルアルコール 10％液 （重合度 500、鹸化度 90％）	40
水	20

##### (2) 顕色性化合物分散液 B の調製

成分	量（重量％）
4, 4'-ジヒドロキシジフェニルスルホン	40
ポリビニルアルコール 10％液 （重合度 500、鹸化度 90％）	40
水	20

【0026】

##### (3) 増感剤分散液 C の調製

成分	量（重量％）
シュウ酸ジ- <i>p</i> -メチルベンジルエステル	40
ポリビニルアルコール 10％液 （重合度 500、鹸化度 90％）	40
水	20

##### (4) 保存性向上剤分散液 D の調製

成分	量（重量％）
4-(2-メチルグリシジルオキシ)-4'-ベンジルオキシジフェニルスルホン	40
ポリビニルアルコール 10％液 （重合度 500、鹸化度 90％）	40
水	20

これらの組成物を縦型サンドミル（アイメックス（株） 30 製、サンドグラインダー）にて別個に分散した。

##### (5) 顔料分散液 E の調製

成分	量（重量％）
軽質炭酸カルシウム （白石中研社製、ブリリアント 15）	40
ヘキサメタリン酸ソーダ 0.7％溶液	60

この組成物をカウレス分散機で分散した。

【0027】さらに分散物 F 液として 20％ステアリン酸亜鉛分散物と分散物 G 液として 20％ステアリン酸アミド分散物および接着剤 H として 49％のスチレン-ブタジエンラテックス（住友ダウ社製、商品名 P O Y 7 40 2）と接着剤 I として 10％澱粉-酢酸ビニルグラフト共重合樹脂（日澱化学社製、商品名 ペトコート c 8）を用意した。これらの分散物・接着剤を用いて乾燥後の重量比率が、A : B : C : D : E : F : G : H : I = 10 : 20 : 20 : 3 : 22 : 5 : 5 : 10 : 5 となるように配合して塗工液とした。この塗工液をロッドブレード法によって前述の下塗り層上に 6 g / m<sup>2</sup>（乾燥）塗工し、感熱発色層を形成した。

#### 【0028】保護層の形成

接着剤樹脂（A、B）として、重合度 1700、鹸化度 50

99.5％ポリビニルアルコール（（株）クラレ製、商品名 O T P 4 H）、アクリルエマルジョン樹脂（三井東圧製、商品名 バリアスター B 1 8 5.0）、顔料（C）として微粉珪酸（水沢化学製、商品名 ミズカシル P 6 0 3）、さらに 20％ステアリン酸亜鉛（D）を用いて乾燥重量比率が A : B : C : D = 40 : 10 : 40 : 10 となるように保護層塗液を調製し、これを先に形成した感熱発色紙の感熱発色層上にロッドブレードで 2 g / m<sup>2</sup>（乾燥）塗布、乾燥後、水分 5～8％、線圧 80 K g / c m でカレンダー掛けを行い感熱記録材料を作成した。

#### 【0029】比較例 1

実施例 1 中の下塗り層の澱粉-酢酸ビニルグラフト共重合樹脂 20 重量％溶液（日澱化学社製、商品名 ペトコート c 8）38 重量％を 18 重量％とし、焼成クレ-（エ

ンゲルハート社製、商品名アンシレックス 93) を 55 重量%とした以外、同様の処理を行なって感熱記録材料を作成した。

#### 【0030】比較例 2

実施例 1 中の保護層の重合度 1700、鹼化度 99.5% ポリビニルアルコール (株)クラレ製、商品名 O T P 4 H) 40 重量%を 15 重量%とし、微粉珪酸 (水沢化学製、商品名ミズカシル P 603) を 40 重量

%から 65 重量%とした以外、同様の処理を行なって感熱記録材料を作成した。

#### 【0031】比較例 3

比較例 1 と同様の下塗り層と比較例 2 と同様の保護層を組み合わせた以外、実施例 1 と同様の処理を行なって感熱記録材料を作成した。

#### 【0032】

#### 【表 1】

	感 度	耐ポリ塩化ビニルラップ性 (保存率%)	印刷水負け評価	ドライピックの評価
実施例 1	1. 3 3	9 8	○	○
比較例 1	1. 3 2	9 3	○	×
比較例 2	1. 1 1	6 5	×	○
比較例 3	1. 1 5	6 1	×	×

【0033】保護層の接着剤樹脂として重合度 1000 以上、鹼化度 98%以上のポリビニルアルコールを 20 から 50 重量部含み、且つ下塗り層の接着剤樹脂として水溶性樹脂を澱粉-ポリ酢酸ビニルグラフト共重合体及び又はその部分鹼化物を 10 から 30 重量部含有することによって、高感度で保存性が良く、耐ビッキング性のあるオフセット印刷適性の良好なものが得られた。

【0034】感度測定 : 実機感熱ファクシミリを試験用に改造したものをを用いて測定した。1ライン記録時間 10ms/ライン、走査線密度 8\*8ドット/mmの条件でパルス幅を変調し、ドット当りの印加エネルギーを 0.5ms に調整し、64ラインの印字を行った。その際の発色濃度をマクベス濃度計 RD-514 で測定し、記録感度を代表する値とした。

【0035】耐ポリ塩化ビニルラップ性 : 記録感度を評価した印字物をポリ塩化ビニルラップフィルムに貼付け、更にその上からポリ塩化ビニルラップフィルムで覆い 40℃で 1 週間経過後の印字濃度をマクベス濃度計 RD-514 で測定した。印字濃度の変化から保存率を算

出し、耐ポリ塩化ビニルラップ性の程度を評価した。

【0036】印刷水負け試験 : 明製作所 RI テスターを用い、インキは東華色素ベストキュアー RNC-紅 (タック 6) でインキ 0.25g に水 0.5cc を加え、インキ練りローラーで 1 分間インキと水を練り、インキを乳化させた後、印刷試験を行って評価を行った。

○ 良好にインキが紙に転移した

× インキの転移が適切でなかった

【0037】ドライピック試験 : 明製作所 RI テスターを用い、インキは東華色素ベストキュアー RNC-紅 (タック 15) でインキ 0.25g を加え、インキ練りローラーで 1 分間インキと水を練り、

インキを乳化させた後、印刷試験を行った。

○ 印刷時に塗膜が剥離しなかった

× 印刷時に塗膜が剥離しなかった

#### 【0038】

【発明の効果】本発明によって、高感度で保存性が良く、耐ビッキング性のあるオフセット印刷適性の良好なものを製造することが可能となった。

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